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Hybrid sensible/thermochemical solar energy storage concepts based on porous ceramic structures and redox pair oxides chemistry

C. Agrafiotis*, M. Roeb, C. Sattler

German Aerospace Center (DLR), Linder Hoehe, Cologne, 51147, Germany

Abstract

The enthalpy effects of reversible chemical reactions can be exploited for the so-called thermochemical storage of solar energy. Oxides of multivalent metals in particular, capable of being reduced and oxidized under air atmosphere with significant heat effects are perfect candidates for air-operated Concentrated Solar Power plants since in this case air can be used as both the heat transfer fluid and the reactant (O_2) and therefore can come to direct contact with the storage material (oxide).

Based on the characteristics of the oxide redox pair Co_3O_4/CoO as a thermochemical heat storage medium and the advantages of porous ceramic structures like honeycombs and foams in heat exchange applications, the idea of employing such structures either coated with or entirely made of a redox material like Co_3O_4 , as a hybrid sensible-thermochemical solar energy storage system in air-operated Concentrated Solar Power plants has been set forth and tested. At first, small-scale, redox-inert, cordierite foams and honeycombs were coated with Co_3O_4 and tested for cyclic reduction-oxidation operation via Thermo-Gravimetric Analysis. Such Co_3O_4 -coated supports exhibited repeatable operation within the temperature range 800–1000°C for many cycles, employing all the redox material incorporated, even at very high redox oxide loading levels. To improve the volumetric heat storage capacity of such reactors, ceramic foams made entirely of Co_3O_4 were manufactured. Such foams exhibited satisfactory structural integrity and were comparatively tested vs. the “plain” Co_3O_4 powder and the Co_3O_4 -coated, cordierite supports under the same cyclic redox conditions up to 15 consecutive cycles. The Co_3O_4 -made porous foams were proved also capable of cyclic reduction–oxidation, exploiting the entire amount of Co_3O_4 used in their manufacture, maintaining simultaneously their structural integrity.

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Keywords: solar energy; thermochemical heat storage; redox reactions; cobalt oxide; structured reactors, ceramic honeycombs, ceramic foams

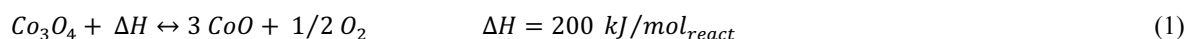
* Corresponding author. Tel.: +49 2203 6014132; fax: +49 22036014072

E-mail address: christos.agrafiotis@dlr.de

1. Introduction

One of the main differences between CSP and other renewable energy technologies is the potential for Thermal Energy Storage (TES) integrated in a CSP plant, i.e. its inherent capacity to store heat for short periods of time for later conversion to electricity when clouds block the sun or after sundown [1]. There are three types of implementing this TES approach, based on the “nature” of heat to be stored: sensible, latent and thermochemical heat [2, 3]. Thermochemical Storage of solar heat exploits the heat effects of reversible chemical reactions for the storage of solar energy [4]. Solar heat produced during on-sun operation by a solar concentrator is used to power an endothermic chemical reaction; if this reaction is completely reversible the thermal energy can be entirely recovered by the reverse reaction taking place during off-sun operation and supplied to the power generation block just like in the case of on-sun operation. Since the oxidation/reduction reactions of several oxides of multivalent metals are accompanied by significant heat effects, such redox oxides can be used to thermochemically store and release solar heat in Concentrated Solar Power Plants using air as heat transfer fluid.

Among oxides of multivalent metals for which their redox reactions are accompanied by significant heat effects, the pair of cobalt oxides $\text{Co}_3\text{O}_4/\text{CoO}$ is one of the most attractive for Thermochemical Storage, since its endothermic reduction (Eq. 1) takes place in air at about 900°C [5] and its energy density is among the highest, 844 kJ/kg [6, 7]:



The theoretical maximum value of weight loss of the forward reaction is 6.64 wt %. Screening Thermo-Gravimetric Analysis (TGA) experiments by the present authors have demonstrated that the redox pair of cobalt oxides $\text{Co}_3\text{O}_4/\text{CoO}$ can operate in a completely reversible, cyclic redox mode within the temperature range $800\text{--}1000^\circ\text{C}$ [8].

On the other hand, the preferred heat storage type for central receiver power plants using air as a heat transfer medium is via sensible heat. Such storage systems exploit the industrially proven technology of high-temperature TES systems, commonly known as regenerators or recuperators [9]. For example, the sensible heat storage concept and technical implementation details of the Solar Tower power plant of Jülich (STJ) Germany, has been described in detail in several publications. The storage system consists of a rectangular housing of $7\text{m} \times 7\text{m} \times 6\text{m}$ size [10, 11]. Instead of pursuing a monolithic design, its volume is partitioned into four chambers of identical size, connected in parallel through a dome and connecting pipes (Fig. 1a). Each chamber is filled with an array of ceramic storage material with which the air exchanges heat and transfers its enthalpy as it flows through it. Comparative studies among many storage medium configurations, like packed beds of broken basalt or ceramic spheres, ceramic saddles, checker bricks etc. (Fig. 1b), have culminated to materializing finally the storage medium as a modular array of flow-through ceramic honeycombs (Fig. 1c) that provide a large heat exchange surface between the air and the solid storage medium [12]. At rated operation conditions, the storage system is cycled between 120 and 680°C , i.e. during on-sun operation (“charging” phase) “hot” air is supplied from the solar tower to the top of the storage medium at a temperature of approximately 680°C - however, if needed, this temperature can be exceeded in future such plants with the same technology - and exits at the bottom at a temperature approximately 120°C . During off-sun operation (“discharging” phase) the air flow is reversed: “cold” air is introduced through the lower end of the already “hot” storage medium to be heated by that as it flows towards its top end, before being introduced again to the steam/power block. The technology is simple in operation but the full load discharge period of this assembly is limited to about 1.5 hours with the total volume of the inventory being relatively large, $\approx 120 \text{ m}^3$.

Based on these characteristics and stemming from the establishment of structured reactors based on porous ceramics like honeycombs and foams in a plethora of chemical reaction and heat exchange applications [13], the idea of employing such ceramic structures coated with or manufactured entirely from such a redox oxide material has been set forth by the present authors [14] and is currently under testing at various levels [8, 15]. By simply coating the currently existing redox-inert honeycombs in STJ with Co_3O_4 (or any other redox oxide system capable of operating within the particular temperature range) or eventually manufacturing them entirely of it, the current sensible solar heat storage concept implemented with chemically-inert porous ceramic structures can be transformed to a “hybrid” sensible-thermochemical one with enhanced efficiency. In fact such redox-oxide-coated [16,17] or redox-oxide-made [18,19] porous ceramic structures have been already employed in “Solar Chemistry” applications

exploiting redox-oxide-based thermochemical cycles for the production of solar fuels. Honeycombs are characterized by their cpsi (cells per square inch) number and foams by their ppi (pores per linear inch) number: higher cpsi/ppi numbers mean “denser” structures with thinner channel walls/struts and more, but smaller, air flow channels per cross-section area unit, i.e. higher gas-solid contact area per unit volume. Ceramic foams in particular provide for “...a considerable degree of radial mixing, which is an advantage in processes limited by heat transfer and can even out flow distribution...” [20]. Such reticulated porous ceramic foams manufactured entirely from cerium oxide (CeO_2) were prepared and tested from the Swiss Federal Institute of Technology/Paul Scherrer Institute (ETH/PSI) Zurich, group for carbon dioxide splitting [21]. More recently, monolithic ceramic bodies - perforated pellets - made of cobalt and of manganese oxides were employed for thermochemical storage applications like the ones addressed in the present study by the group of Aerosol and Particle Technology Laboratory (APTL), of CERTH, Thessaloniki, Greece [22].

2. Experimental

Based on our results on “plain” powders reported previously [8], two raw Co_3O_4 oxides from different suppliers, namely Materion Advanced Chemicals (Milwaukee, USA) and Beijing Cerametek Materials Co., Ltd. (Beijing, China) were employed in this study, hereafter to be referred as powders No1 and No2, respectively. Powder No1 was employed for the coating of the porous supports whereas Powder No2 for the manufacture of the foams. The physical/chemical characteristics of the powders have been reported therein. Based on those findings, the current work involved tests only between 985-785°C with a ramp (heating/cooling) rate of 5°C/min and no dwell at either the higher or the lower temperature since both Co_3O_4 powders were found to exhibit stoichiometric, long-term, cyclic reduction-oxidation under these conditions.

For the manufacture and testing of Co_3O_4 -coated porous structures, at first mini-specimens of redox-inert cordierite foams and honeycombs of dimensions such that could be accommodated within the TGA holder/chamber were sectioned from commercial pieces of larger dimensions. Coating was performed by their impregnation in Co_3O_4 powder slurries under stirring, subsequent drying at 110°C and calcination at 800°C for 4 hours with the rationale on one hand to induce adequate adhesion of the redox coating on the supports and on the other hand not to exceed the redox temperature of Co_3O_4 (identified as $\approx 885^\circ\text{C}$). Loading percentage was determined from the increase of specimen weight after final calcination and is referred throughout as wt. % i.e. as mass of redox material coated per mass of the initial “bare, dry support. Coated specimens with various loading percentages were obtained by repeating the above procedure for several times.

To improve the volumetric heat storage capacity, the next step involved manufacturing entire porous monolithic objects – foams - from the Co_3O_4 redox material, prepared by the PolyUrethane (PU) foam replica method [23]. PU foam specimens of 30 and 45 ppi were sectioned from larger samples and impregnated also in Co_3O_4 powder slurries. The loaded specimens were withdrawn and excess slurry was removed by blowing air via an air-gun through their structure. Then the specimens were dried at 110°C overnight and finally placed in alumina boats and calcined in a tubular furnace under air atmosphere. Since the redox behavior of Co_3O_4 is fully reversible, calcination temperatures higher than the redox temperature can be employed: the material is completely transformed from Co_3O_4 to CoO upon heating and crossing the redox temperature of 885°C and back to Co_3O_4 from CoO upon cooling from the sintering temperature when crossing the redox temperature again. Various sintering temperatures were thus tested; it was found that in order to obtain satisfactorily rigid foams a sintering temperature of at least 1300°C was eventually required (significantly lower though than the melting point of Co_3O_4 which is 1935°C).

3. Results – Discussion

Typical cordierite mini-honeycombs and foams employed in this work are shown on the TGA holder in Figure 2 in three different states: “bare” before their coating, after being Co_3O_4 -coated but prior of being tested in the TGA and finally after such cyclic TGA tests. The “raw” weight change results of such experiments with coated specimens correspond to the variation of the weight of the entire Co_3O_4 -loaded support. Since the supports are redox-inert unless other side reactions take place, this weight change is attributed entirely to the redox material, Co_3O_4 . Since the loading percentage on each support is measured from the weight increase after calcination, a second weight

change curve can be constructed, corresponding to the weight change calculated as a percentage of the initially loaded Co_3O_4 powder. This quantity provides a measure of how much of the loaded Co_3O_4 powder has been exploited for the redox reactions, since its maximum possible value is the one calculated from the stoichiometry of reaction (1) above, as the oxygen release/uptake i.e. 6.64 wt %. Therefore, two different curves are plotted for each coated specimen: the weight change of the whole coated porous support (solid lines) and the weight change calculated as a percentage of the redox material actually coated on it (dotted lines, same colour). In all cases these are compared to the respective curve of the “plain” Co_3O_4 powder No1 (solid blue line).

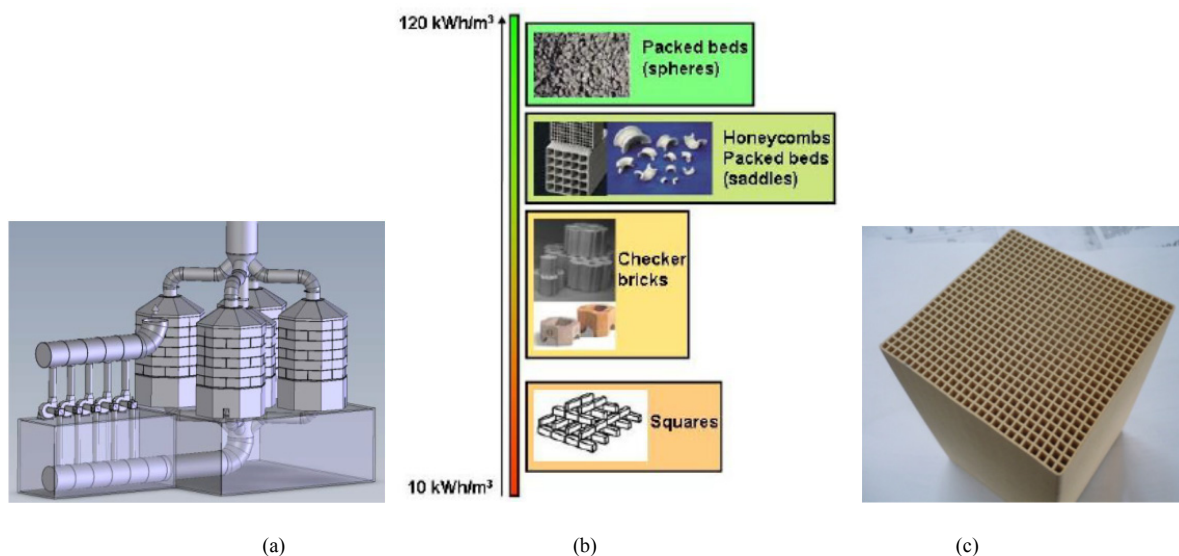


Fig 1. (a) View of current TES sensible heat concept in STJ; (b) inventory materials considered before decision in favor of ceramic honeycombs in an orthogonal shaped containment; (c) actual ceramic honeycomb employed (length x width x height: 150mm x150mm x300mm) (From [11]).

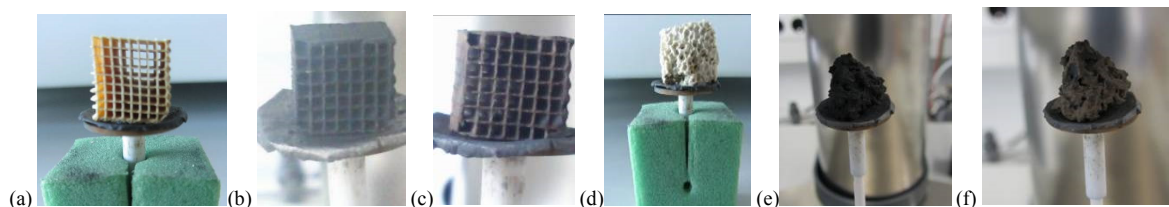


Fig 2. From left to right: Typical cordierite mini-honeycombs (a)-(c) and foams (d)-(f) on the TGA holder before coating, after coating and after TGA cyclic redox cycling respectively.

The results (weight change and temperature curves vs. time) for three cordierite honeycombs coated with various loading percentages of Co_3O_4 (from ≈ 17 -94 wt %) are shown in Fig. 3 compared to the respective behavior of the “plain” Co_3O_4 powder. All these experiments were run for 2 cycles. Longer-term respective results for two cordierite foams coated with Co_3O_4 loading percentages of 13 and 64 wt % are shown in Fig. 4. The experiments for the plain powder and one foam were run for 30 cycles; that for the other foam for 15 cycles. The entire experiments are depicted in Fig. 4a, to provide an idea of the reproducibility from cycle to cycle, whereas in Fig. 4b only the “magnifications” of cycles 1-2 and 12-15 are shown to clarify and delineate the important characteristics.

It is evident that for all coated oxide supports tested, the weight loss calculated per mass of the coated powder is practically equal to that of the “plain” powder and the theoretical maximum value of 6.64 wt %. In other words all the redox material loaded on the supports is exploited for cyclic reduction-oxidation. In addition, from the

photographs in Fig. 2 it is also obvious that the coated structures have maintained their structural integrity without showing any evidence of coating detachment or spallation.

The next step was the manufacture and testing of entirely- Co_3O_4 -made foams. Such foams weighted between 0.5–1.5 g. A characteristic photograph of such small-size foam pieces sintered at 1300°C for 4 hrs is shown in Fig. 5a. Respective digital micrographs of a 30 ppi foam are shown in Figs. 5b, 5c and SEM photographs in progressively higher magnifications in Figures 5d–5f. The characteristic triangular foam struts are clearly visible. The particular foams are characterized by a dual-scale porosity: in addition to the “large” circular pores defined by the struts, the struts themselves are not dense, but porous. This is obviously due to the relevantly low sintering temperature of 1300°C employed; the strut porosity can be further “tuned” by varying the sintering temperature.

The same results (weight change and temperature curves vs. time) for two Co_3O_4 -made foams, one 30 and one 45 ppi, are shown in Fig. 6 compared to the behaviour of the respective, “plain”, as-received Co_3O_4 powder No2 used for their manufacture (orange line). The experiments for the powder and the 45 ppi foam were run for 2 cycles; that for the 30 ppi foam for 15 cycles. From the photographs of the foams before and after redox cycling shown in Figs. 7a–d it is evident that the foams did not exhibit any cracking after the experiment maintaining completely their structural integrity. Fallen-off powder, cracking or disruption of the foams, are not visible. It is obvious that in both structured specimens almost all the amount of redox powder used for their manufacture is employed for the redox reaction. During the first cycles the maximum weight difference between the reduced and the oxidized state is similar for the two foams, slightly lower than the stoichiometric percentage, ranging around 6 %. However with increasing number of cycles, the “top” of the curve is slightly shifted to higher values and this difference stabilizes and approaches the one for the “plain” powder, to about 6.5 %.

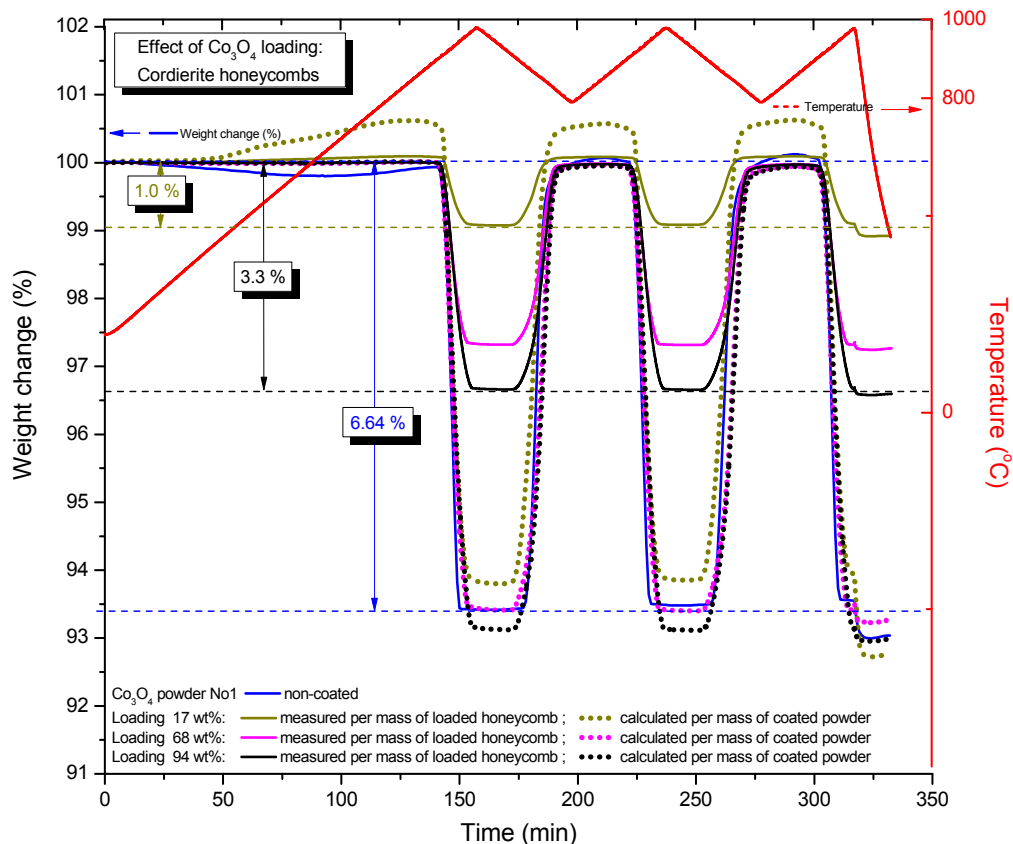


Fig 3. Effect of loading on redox performance of Co_3O_4 -coated cordierite honeycombs, 2-cycle experiments.

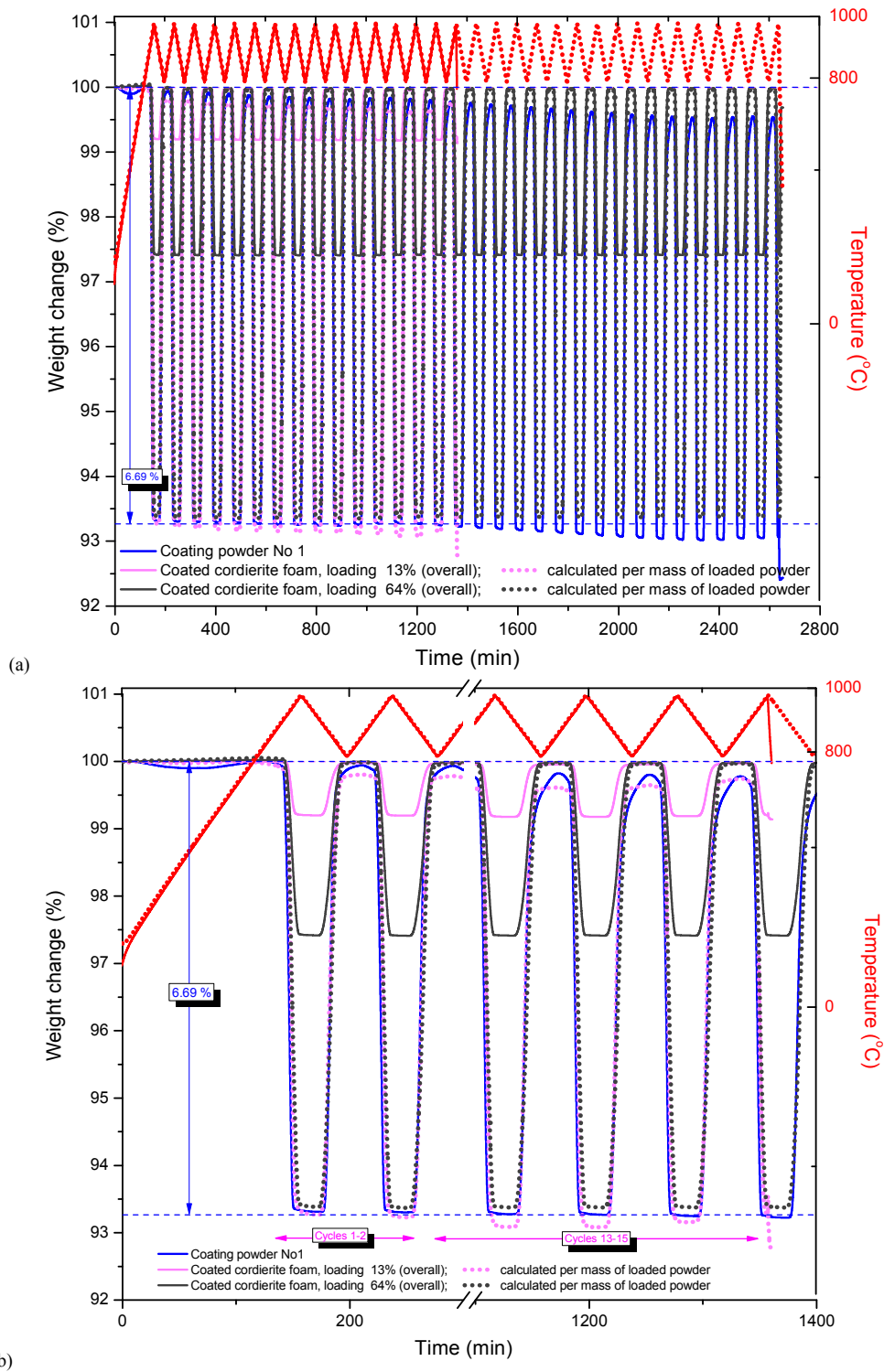


Fig 4. Effect of loading and long-term cycling on redox performance of Co_3O_4 -coated cordierite foams: (a) entire experiments: foam loaded 13. wt % for 15 cycles and foam loaded 64 wt % for 30 cycles; (b) "magnification" of cycles 1-2 and 12-15.

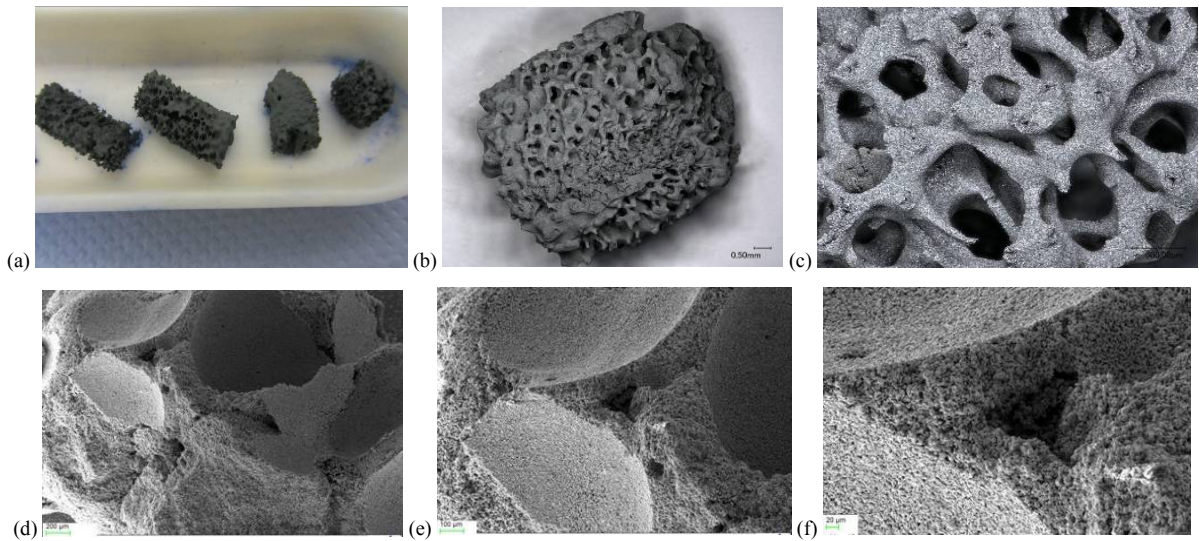


Fig 5. Macro- and micro-structure of a 30 ppi foam made entirely of Co_3O_4 calcined at 1300°C for 4 hrs.

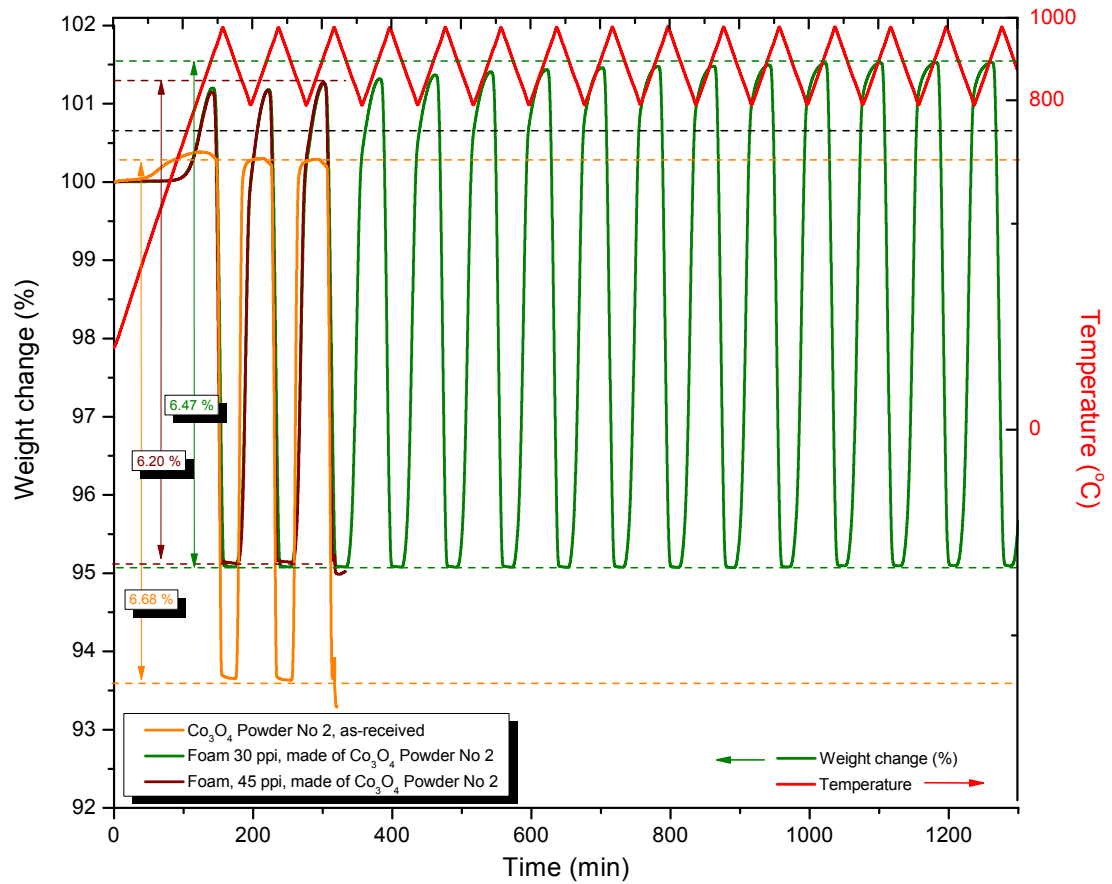


Fig 6. Cyclic redox experiments of foams made entirely of Co_3O_4 vs. respective “plain”, as-received Co_3O_4 powder used for their manufacture.

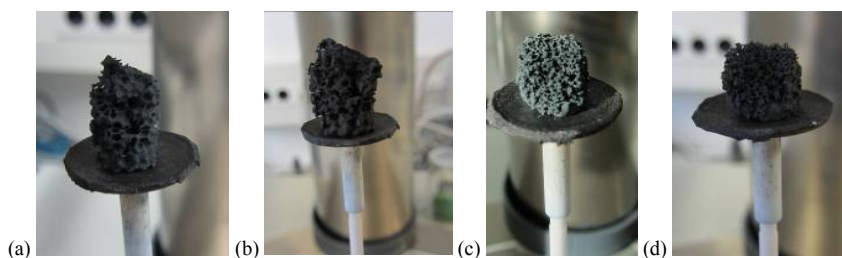


Fig 7. Photographs of the two foam specimens on the TGA holder demonstrating their macro-structural integrity before and after the end of the respective experiments: (a), (b) 30 ppi foam before/after 15 cycles; (c), (d) 45 ppi foam before/after 2 cycles.

Both, the “plain” powder No2 and to a higher extent the foams made of it, exhibited a slight increase in weight during the initial heat-up stage before the onset of reduction. This is characteristic indication of oxidation of possible traces of the reduced phase CoO existing in the material. With respect to the foams in particular, this existence of CoO can be due to the in-situ reduction of Co_3O_4 by the organic material of the PU foam during pre-TGA-calcination. Indeed, comparative XRD analysis of the as-received powder and of a powder sample obtained after crashing small pieces of the as-synthesized foams shown in Figure 8 revealed that the foam in its as-synthesized state (prior to the cyclic TGA process) contains a minor, yet XRD-detectable percentage of CoO.

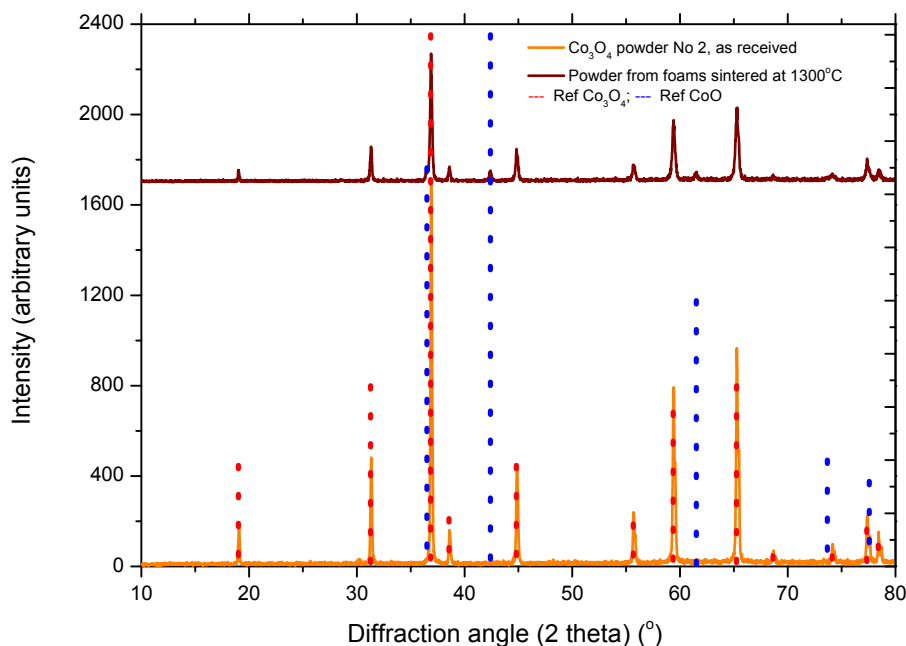


Fig 8. XRD comparison between as-received Co_3O_4 No2 powder and of a powder obtained after crashing pieces of the calcined foams made of it.

To further clarify the effect of organics on the phase composition of the redox structure before cyclic TGA redox testing, several pellets were made of Co_3O_4 powder No2 (the same from which the foams were made of) employing a small quantity of organic binder necessary for their shaping. The pellets were subsequently calcined under the same schedule as the foams (i.e. at 1300°C for 4 hrs) together with “plain” powder No2 (which had no addition of any organics). After calcination, all these samples were subjected to 2-cycle TGA redox experiments. The weight change results are shown in Fig. 9 where also the respective maximum weight differences between the reduced and the oxidized states are marked. The effect of initial amount of organics (which results in possible initial traces of CoO in the initial samples) is evident: the foam that contained the most organics prior to calcination has the

maximum “deflection” above the 100% wt (i.e. contains initially the most CoO which is oxidized prior to reduction). On the contrary the “plain” powder after calcination at 1300°C contains no traces of any pre-existing CoO, thus its weight curve prior to the onset of reduction is practically flat. The curve for the pellet (blue line) is somewhere in-between. In any case, such deviations are small and do not affect the overall performance of the specimens, since complete oxidation of any structured specimen during pre-calcination can be ensured by proper “fine-tuning” of the sintering conditions – a subject currently under investigation.

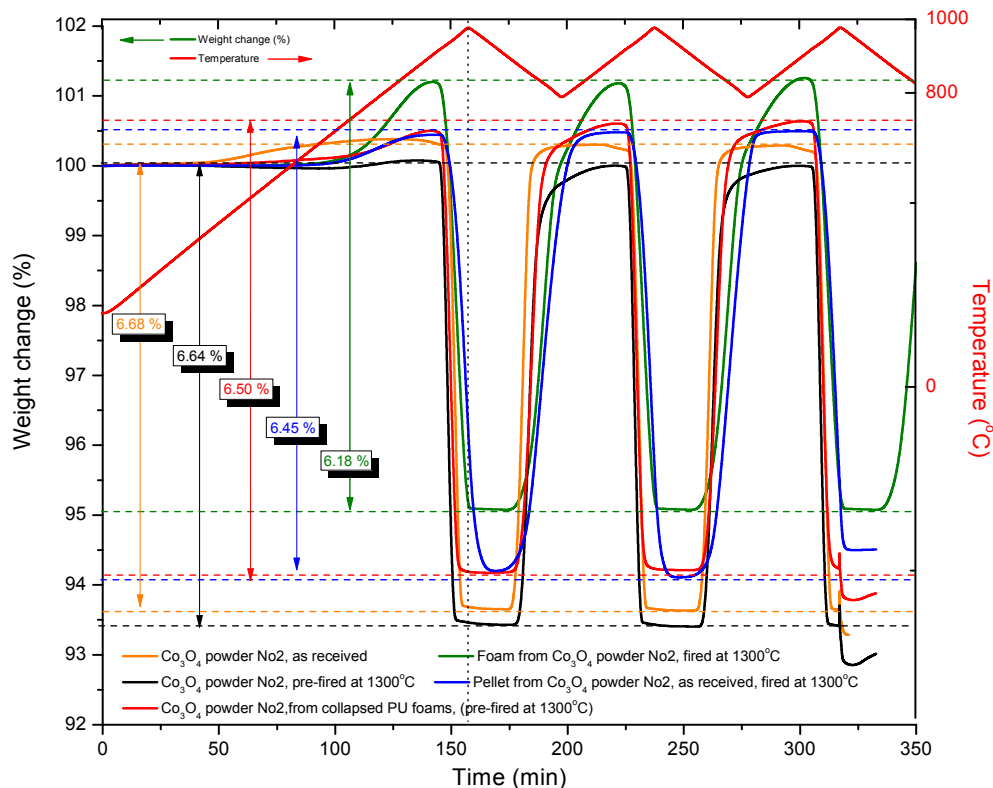


Fig 9. Weight change comparison during TGA reduction/oxidation among all Co_3O_4 No2 “products” calcined at 1300°C, with different amounts of organics initially present in their composition.

4. Conclusions

The idea of combining the attractive thermochemical characteristics of the oxide redox pair $\text{Co}_3\text{O}_4/\text{CoO}$ with the inherent features of porous ceramic supports in a novel, compact, hybrid sensible-thermochemical storage, reactor-heat exchanger for air-operated solar power plants was implemented and investigated. In this perspective, at first, lab-scale, redox-inert, cordierite foams and honeycombs were coated with a variety of Co_3O_4 loading percentages, from 13 to ≈ 97 wt %. These structures were subsequently tested for cyclic reduction-oxidation in a TGA apparatus within the temperature range 800–1000°C in comparison to “plain” Co_3O_4 powder. Irrespective of the loading percentage, the entire amount of the redox material coated was employed for the redox reactions, as inferred from the weight loss and re-gain recorded per weight of redox material loaded on the supports, which corresponded to full reduction/oxidation of the two cobalt oxide states. No detrimental interactions of the redox coating with the cordierite support was observed. All coated structures maintained their structural integrity whereas in addition no coating spallation or detachment was observed even after long-term operation of up to 30 consecutive cycles.

Subsequently the manufacture of small-scale ceramic foams entirely of Co_3O_4 was successfully demonstrated. Such foams were comparatively tested vs. the loaded porous structures as well as vs. “plain” Co_3O_4 powder. These

monolithic, porous, structured specimens were capable of cyclic redox operation, also eventually exploiting for the thermochemical reactions almost the entire amount of oxide used for their manufacture. Small deviations of stoichiometry observed in the first cycles were attributed to partial reduction of Co_3O_4 from organic compounds during pre-TGA sintering. Foams were tested for up to 15 redox cycles, maintaining simultaneously their structural integrity and stoichiometric reduction/oxidation performance.

Such porous foams are thus considered as an elegant technical solution for further scale-up of the proposed concept to compact, integrated hybrid sensible-TCS reactor/heat exchanger configurations, with enhanced volumetric heat storage capacity, transport, thermal and heat recovery properties. Current research is focused on the manufacture of larger-scale porous structures and their evaluation in conjunction to a real solar facility.

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